

Stability of hydrogenated group-IV nanostructures: magic structures of diamond nanocrystals and Silicon quantum dots

Xiaobao Yang,^{1,*} Hu Xu,² Yu-Jun Zhao,¹ and Boris I. Yakobson³

¹*Department of Physics, South China University of Technology, Guangzhou 510640, People's Republic of China*

²*Center of Super-Diamond and Advanced Films (COSDAF) Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, China*

³*Department of Mechanical Engineering and Materials Science, Department of Chemistry, and The Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, Texas 77005, USA*
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We have developed an effective model to investigate the energetic stability of hydrogenated group-IV nanostructures, followed by validations from first-principles calculations. It is found that the Hamiltonian of X_mH_n ($X=C, Si, Ge$ and Sn) can be expressed analytically by a linear combination of the atom numbers (m, n), indicating a dominating contribution of $X-X$ and $X-H$ local interactions. As a result, we explain the stable nanostructures observed experimentally, and provide a reliable and efficient technique of searching the magic structures of diamond nanocrystals(Dia-NCs) and Silicon quantum dots(SiQDs).

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Semiconductor nanocrystals have been greatly attractive and intensively investigated[1, 2]. These nanomaterials extend the physics of reduced dimensions and offer the opportunity for fundamental study of the regime between nanostructure and bulk states[3], which have also brought wide applications as nanoscale electronic and optical devices[4], fluorescent biological labels[5], quantum computation media[6] etc. Besides II-VI and III-V semiconductor compounds[7], various hydrogenated group-IV (C[8, 9], Si[10, 11], and Ge[12]) nanocrystals with sp^3 hybridizations have been synthesized and isolated, whose optical response depends on particle size, shape and symmetry. Theoretical studies[13–15], have focused on optical properties of these nanocrystals and employed various methods for accurate calculations of adsorption spectrum.

The determination of stable structures, which dominate the optical properties of nanocrystals[8, 9], is not well understood so far. Previous calculations constructed Dia-NCs[15] according to the synthesis experiments, which indicated that larger members of the series have smaller surface-to-volume ratios and lower hydrogen-to-carbon ratios[8]. According to the Wulff energy, the polycrystalline wire of five-fold symmetry is more stable than single-crystal types[16], for silicon nanowires with the diameter less than 6 nm. Recent studies[17, 18] searched the magic structures of silicon nanowires using genetic algorithm, in which the energies are calculated with classical potential in Hansel-Vogel (HV) formulism to reduce the time cost.

It is challenging to determine the stable configuration from numerous possible candidates and there are three main obstacles for searching magic structures of X_mH_n ($X=C, Si, Ge$ and Sn): 1) the accurate calculation of

the total energy is necessary but often computationally expensive; 2) over many isomeric structures should be considered and the number of these structures increases sharply as m and n increase; 3) the minimum of n is not clear for a certain m , though the maximum of n is trivially $2m + 2$.

In this letter, we investigate hydrogenated group-IV nanocrystals by both model analysis and first-principles approaches. We proposed an effective model and gave an analytical expression of the Hamiltonian for X_mH_n ($X=C, Si, Ge$ and Sn) with the numbers of atoms (m, n), as is confirmed by the first-principles calculations. Our finding provides an efficient and reliable avenue of searching magic structures of Dia-NCs and SiQDs, which extends our understanding on experiment observed stable nanocrystals.

In our model, we assume the Hamiltonian of X_mH_n ($X=C, Si, Ge$ and Sn) to be as

$$\mathcal{H} = \sum_{i=1}^m (\mathcal{H}_{\text{int}} + \mathcal{H}_0) - m\mu_X - n\mu_H \quad (1)$$

where \mathcal{H}_{int} and \mathcal{H}_0 are the contributions from interactions and self energies, and $\mu_X(\mu_H)$ is the chemical potential for $X(H)$ atom. The sum runs over all the group-IV atoms and we have $\mathcal{H}_0 = \mu_{X_0} + p_i\mu_{H_0}$, where p_i is the number of H atoms in saturated group of the i th X atom and $\mu_{X_0}(\mu_{H_0})$ is the isolated atomic energy for $X(H)$ atom. \mathcal{H}_{int} includes the energy contributions from bonded X -atom pair ($-E_{X-X}$) and the saturated group of the i th X atom ($-E_{XH_{p_i}}$). As shown in the inset of Fig.1, every X atom has four nearest neighbors and every $X-X$ bond is shared by two X atoms. This leads the energy contribution corresponding to the i th X atom to be $-2E_{X-X}$ for $p_i = 0$, and $-1.5E_{X-X} - E_{XH_{p_i}}$ for $p_i = 1$ analogically. Thus, $\mathcal{H}_{\text{int}} = -(2 - 0.5p_i)E_{X-X} - E_{XH_{p_i}}$.

We assume that the interaction between X and H atoms is localized and thus $E_{XH_{p_i}} = p_iE_{X-H}$, $p_i =$

*corresponding author: scxbyang@scut.edu.cn

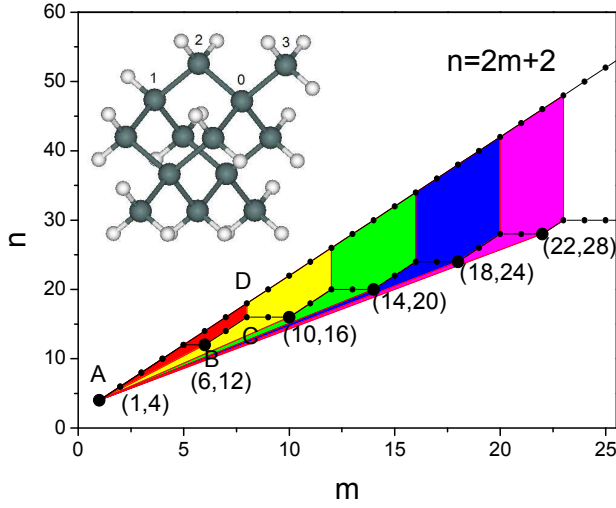


FIG. 1: (Color online) Possible (m, n) for X_mH_n . The convex corresponds to the local minimum and magic structures of hydrogenated nanostructures.

0, 1, 2, 3. With $n = \sum_{i=1}^m p_i$, we found that Eq. (1) can be written as $\mathcal{H} = am + bn$, where $a = (-2E_{X-X} - \mu_X + \mu_{X_0})$ and $b = (-E_{X-H} + 0.5E_{X-X} - \mu_H + \mu_{H_0})$. This implies that the energy of X_mH_n is determined by the interaction strength of $X-X$ and $X-H$, chemical potentials, and the atom numbers (m, n) .

Instead of scanning the parameter space (a, b) [19], the Simplex method[20–22] is efficient to determine the combinations of lowest energy from a set of possible integer combinations (m, n) , which indicates that the stable configurations correspond to corners, edges and faces[22]. We will obtain the ground states if we construct enough restricting inequalities and solve the corresponding linear equations[22]. In our case, we have $m \geq 1$ and $n \leq 2m + 2$. The key task is to determine the lower limit of n for a certain m , for which it is difficult to find out the expected inequalities. We search the least n as follows[23]: i) starting from one of the stochastic configuration of X_mH_n ($n \leq 2m + 2$), exchange X and H atoms and saturate the configuration with H atoms when necessary; ii) we accept the new configuration when the H atom number is non-increasing, otherwise the new geometry will be accepted with the probability of $1/|dn|$, where dn is the increment of H -atom number. We find that n will converge into the minimum after hundreds of iterations.

Figure 1 shows the upper and lower limit of n as a function of m . It is not a standard Simplex because both m and n will be increasing with an increasing nanocrystal size of X_mH_n . However, we will obtain a convex quadrangle ABCD (colored in red) if a restriction of $m \leq 8$ is considered. The convex A (1, 4) and B (6, 12) are corresponding to stable configurations, while C (8, 16) and D (8, 18) are not since they are induced by the artificial restriction of $m \leq 8$. Thus, XH_4 and X_6H_{12} will be stable configurations for group-IV nanocrystals. Ana-

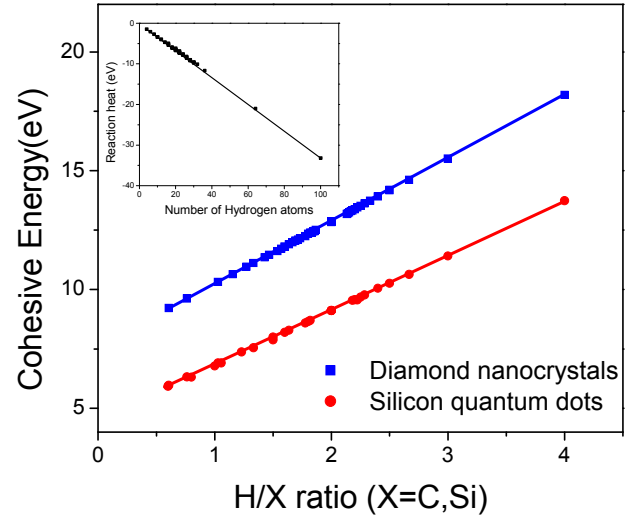


FIG. 2: (Color online) Cohesive energies of Dia-NCs and SiQDs as a function of the $H/(C, Si)$ ratio. Inset shows the linear dependence between the reaction heat of Dia-NCs and hydrogen numbers.

logically, we will obtain a new convex quadrangle (color in red and yellow) and find another stable configuration of $X_{10}H_{16}$ in place of X_6H_{12} , if we consider a restriction of $m \leq 12$. Besides, we find that $X_{14}H_{20}$, $X_{18}H_{24}$ and $X_{22}H_{28}$ are also stable configurations. It should be noted that, except for XH_4 , all other nanocrystals are meta-stable states, since they are local convex ascribed to the size confinement. As is known, the size of nanocrystals increases with increasing reaction time as more material is added to the surfaces.

Till now, we have settled the main obstacles in searching magic structures of group-IV nanostructures according to our model analysis. Firstly, we can estimate the Hamiltonian simply by $E_{tot} = m\mu_{X_0} + n\mu_{H_0} - (2mE_{X-X} - 0.5nE_{X-X} + nE_{X-H})$, since the total energies (E_{tot}) directly obtained from the first-principles calculations do not involve the environment-related chemical potentials and in fact correspond to the Hamiltonian in Eq. (1) with $\mu_X = \mu_H = 0$. Secondly, we should only consider few possible candidates of X_mH_n with various n for a certain m , as isomeric structures with the same chemical formula will possess comparable total energies. Thirdly, we have searched the least n corresponding to a certain m iteratively and determined magic structures by the Simplex method.

To verify the reliability of the above model, we investigate the energetic stability of group-IV nanocrystals (with the example of Dia-NCs and SiQDs) to search the magic structures, using the first-principles method implemented in Vienna Ab initio Simulation Package (VASP)[24, 25]. We use Vanderbilt ultrasoft pseudopotentials[26] and the exchange correlation with the generalized gradient approximation given by Perdew and Wang[27]. We set the plane-wave cutoff energy to be 350 eV and the convergence of the force on each atom

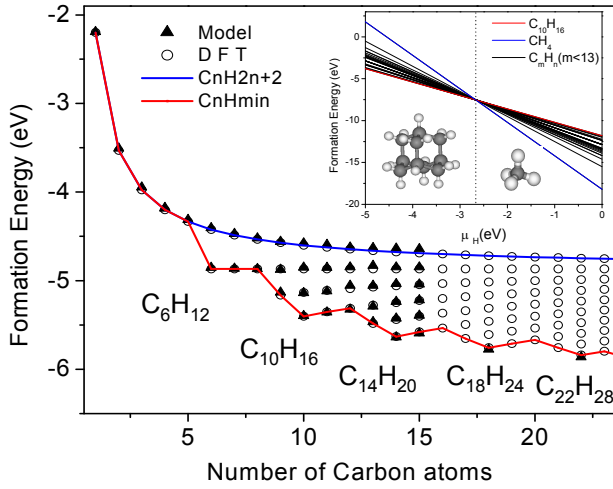


FIG. 3: (Color online) Formation energies as a function of the number of Carbon atoms for diamond nanocrystals with $\mu_H = -4\text{eV}$. Inset shows the chemical phase diagram for C_mH_n with $m \leq 12$.

to be less than $0.01 \text{ eV}/\text{\AA}$ mesh of \mathbf{k} space is used and the vacuum distance is set to be 9 \AA , which is enough to make the systems isolated.

We define the cohesive energy (E_{coh}) per X atom in the nanocrystals X_mH_n as $E_{\text{coh}} = (m\mu_{X_0} + n\mu_{H_0} - E_{\text{tot}})/m$, i.e., $E_{\text{coh}} = 2E_{X-X} - (0.5E_{X-X} - E_{X-H})\alpha$, with α is the H/X ratio (n/m). Figure 2 shows the cohesive energy of X_mH_n ($X=\text{C, Si}$) as a function of the H/X ratio. As predicted, the cohesive energy decreases with the decrease of the H/X ratio following a linear relationship, approaching the value of bulk material ($-\mu_{\text{Diamond-bulk}}=7.65\text{eV}$ and $-\mu_{\text{Si-bulk}}=4.67\text{eV}$ [28]) when the H/X ratio reaches zero. In addition, we can make a deduction that the reaction heat $Q = E_{\text{tot}}(C_mH_n) - E_{\text{tot}}(C_m, \text{Diamond}) - E_{\text{tot}}(H_n, H_2) = n(0.5E_{C-C} - E_{C-H} + 0.5E_{H-H})$ will also have a linear dependence on the H atom number n , confirmed by our calculations (shown in the inset of Fig. 2). Thus, the interaction in X_mH_n is dominated by the localized X-X and X-H interactions and the Hamiltonian estimated in the model by $E_{\text{tot}} = m\mu_{X_0} + n\mu_{H_0} - (2mE_{X-X} - 0.5nE_{X-X} + nE_{X-H})$ is at the accuracy level of the first-principles approach.

In the following, we investigate the magic structures of Dia-NCs exemplified by C_mH_n . We calculated the total energies of nanocrystals with carbon atoms $m \leq 12$ and obtained the formation energies as a function of hydrogen chemical potential by $E_f = (E_{\text{tot}} - m\mu_{X_0} - n\mu_{H_0} - n\mu_H)/m$. As shown in the inset of Fig.3, we find that there is a critical point μ_0 ($\mu_0 = 0.5E_{C-C} - E_{C-H} \simeq -2.63\text{eV}$) of chemical potential, at which the formation energies are the same for all these nanocrystals. Below the critical point $C_{10}H_{16}$ is the most stable, while CH_4 is the most stable when μ_H is above the critical point. As predicted, CH_4 and $C_{10}H_{16}$ are stable states when the number of carbon atoms $m \leq 12$.

Figure 3 shows the formation energies for various

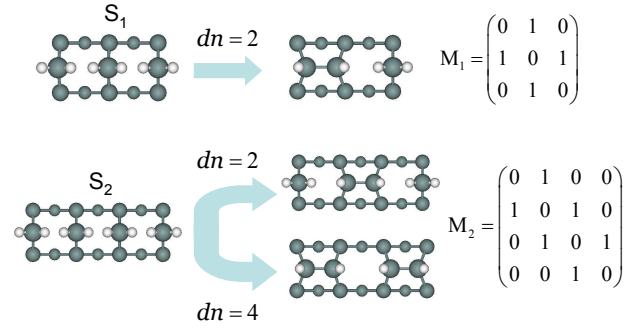


FIG. 4: (Color online) The possible dimer reconstructions and their effect on the number of hydrogen atoms..

C_mH_n with the chemical potential of hydrogen $\mu_H = -4\text{eV}$. The hollow circles are from our model prediction, which is in excellent agreement with the ones from the first-principles calculations (marked with solid triangles). It is noted that the isomeric structures have similar formation energies especially for the chemical potential far away from the critical point, though there are remarkable difference in their total energies. For a certain m , the formation energy decreases as the hydrogen atom number n decreases. The magic structures can be found at the local minimum of the formation energies, such as $C_{10}H_{16}$, $C_{14}H_{20}$, $C_{18}H_{24}$ and $C_{22}H_{28}$. All these structures are consistent with the previous model analysis, which have also been confirmed by experiments[8, 9]. We can also predict that, for the chemical potential $\mu_H > \mu_0$, the formation energy will decrease as the hydrogen atom number n increases for a certain m , thus the stable structures are alkane C_mH_{2m+2} .

For hydrogenated group-IV nanocrystals, magic structures often correspond to the ones with the least or most hydrogen atoms, according to the linear dependence of total energies on H/X ratio. In our previous study[29], we have investigated magic structures of hydrogenated SiQDs, which are in agreement with the ones of Dia-NCs. It is reasonable as our model analysis showed that the magic structures of X_mH_n are the same for all group-IV elements. So far, we have not considered any possible reconstructions, which might induce strain and instability, especially for Dia-NCs with small size. For SiQDs, however, the formation of dimers is common and often dominates the surface reconstruction[11, 16, 30], which will further decrease the hydrogen number. According to our calculations, we find that the E_{coh} of SiQDs with reconstructions also follow the linear dependence on the H/Si ratio.

For simplicity, we consider a dimer reconstruction on (100) facet as is shown in Fig. 4. The hydrogen number of structure S_1 will decrease by 2 when the dimer forms. For structure S_2 , the hydrogen number will decrease by 2 or 4, depending on the selection of Si atoms for reconstructions. To find out the max decrement of hydrogen number, we construct a matrix comprised of 0 and 1 according to the arrangement of Si atoms with $-\text{SiH}_2$: the

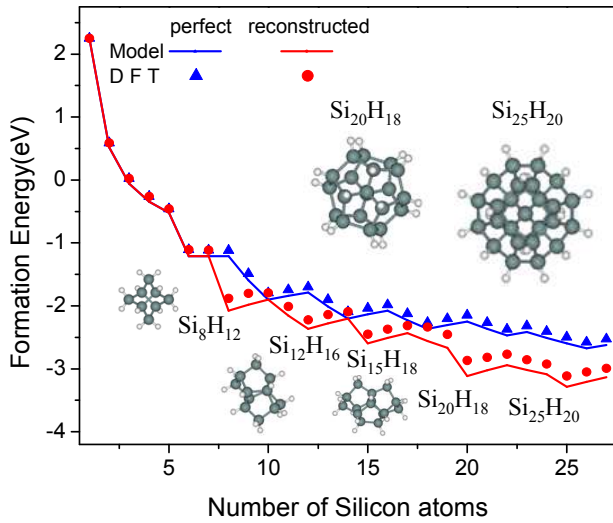


FIG. 5: (Color online) Formation energies as a function of the number of Silicon atoms for SiQDs with and without the dimer reconstructions.

element $M(i, j)$ in the matrix is 1 when a dimer could be formed by the i th and j th Si atoms; otherwise, it is 0. M_1 and M_2 correspond to the structures S_1 and S_2 shown Fig. 4. The max decrement of hydrogen number is equal to the rank of the matrix. It can be comprehensible that the max decrement of hydrogen number is independent of the order of Si atoms, and the rank of matrix is an intrinsic parameter that conserves in the elementary transformations. For SiQDs with various facets, we can construct a block matrix: $M=(M_1, 0, 0; 0, M_2, 0; 0, 0, \dots)$. The max decrement of hydrogen number should be calculated as: $\text{rank}(M)=\text{rank}(M_1)+\text{rank}(M_2)+\dots$. We search the least hydrogen number for SiQDs with a certain num-

ber m through the similar procedure.

Figure 5 shows the formation energies of Si quantum dots with and without dimer reconstructions with $\mu_H = -4\text{eV}$. The dimer reconstruction decreases the formation energies and changes the magic structures. For example, $\text{Si}_{10}\text{H}_{16}$ might not be the magic structure as its formation energy is higher than that of Si_8H_{12} , which can be obtained from Si_8H_{16} with two dimer reconstructions. Besides, $\text{Si}_{12}\text{H}_{16}$, $\text{Si}_{15}\text{H}_{18}$, $\text{Si}_{20}\text{H}_{18}$, and $\text{Si}_{25}\text{H}_{20}$ are new magic structures. The reconstructions also have significant effect on the symmetry of SiQDs. Stable SiQDs without reconstructions tend to be octahedron enclosed by (111) facet, e.g. $\text{Si}_{35}\text{H}_{36}$. However, the reconstructed $\text{Si}_{20}\text{H}_{18}$ has the symmetry of C_{3v} and $\text{Si}_{25}\text{H}_{20}$ is approximately spherical.

In summary, we have proposed an effective method for investigating the stability of H-terminated group-IV nanostructures. We express the Hamiltonian of $X_m\text{H}_n$ ($X=\text{C}, \text{Si}, \text{Ge}$ and Sn) into the linear combination of the atom numbers and obtained the total energies with high reliability. We find that the isomeric structures are nearly energetically degenerated and the stable structures correspond to the ones with the least or most hydrogen atoms. The predicted stable Dia-NCs are in good agreement with experimental observations. With the overcome of the bottlenecks for stability determination, our model provides an efficient technique of searching magic structures.

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